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Research Contract N00014-90-J-1178

R&T Code 413r008---001

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TECHNICAL REPORT No. 12

LUMINESCENCE AND ABSORPTION SPECTRA OF  $C_{60}$  FILMS

by

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Submitted to

*Physical Review Letters*

DTIC  
ELECTE  
FEB 27 1991  
S B D

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Los Angeles, CA 90024-1569

February, 1991

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## REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION <b>UNCLASSIFIED</b>			1b RESTRICTIVE MARKINGS <b>N/A</b>	
2a SECURITY CLASSIFICATION AUTHORITY <b>N/A</b>			3 DISTRIBUTION / AVAILABILITY OF REPORT  <b>Approved for public release; distribution unlimited</b>	
2b DECLASSIFICATION / DOWNGRADING SCHEDULE <b>N/A</b>				
4. PERFORMING ORGANIZATION REPORT NUMBER(S)  <b>N/A</b>			5 MONITORING ORGANIZATION REPORT NUMBER(S)	
6a NAME OF PERFORMING ORGANIZATION <b>The Regents of the University of California</b>		6b OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION <b>1) ONR Pasadena - Administrative 2) ONR Alexandria - Technical</b>	
6c ADDRESS (City, State, and ZIP Code) <b>Office of Contracts &amp; Grants Administration U C L A, 405 Hilgard Avenue Los Angeles, CA 90024</b>			7b ADDRESS (City, State, and ZIP Code) <b>1) 1030 E. Green Street, Pasadena, CA 91106 2) 800 N. Quincy St., Arlington, VA 22217-5000</b>	
8a NAME OF FUNDING / SPONSORING ORGANIZATION <b>Office of Naval Research</b>		8b OFFICE SYMBOL (If applicable) <b>ONR</b>	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER <b>N00014-90-J-1178</b>	
8c ADDRESS (City, State, and ZIP Code) <b>800 N. Quincy Street, 614A:DHP Arlington, VA 22217-5000</b>		10 SOURCE OF FUNDING NUMBERS		
		PROGRAM ELEMENT NO	PROJECT NO	TASK NO
		WORK UNIT ACCESSION NO		
11. TITLE (Include Security Classification) <b>UNCLASSIFIED: LUMINESCENCE AND ABSORPTION SPECTRA OF C<sub>60</sub> FILMS</b>				
12 PERSONAL AUTHOR(S) <b>C. Reber, L. Yee, J. McKeirnan, J.L Zink, R. Stanley Williams, W.M. Tong, D.A.A. Ohlberg and R.L. Whetten</b>				
13a TYPE OF REPORT <b>Tech.Rpt. #12</b>		13b TIME COVERED <b>FROM June '90 TO Feb '91</b>		14 DATE OF REPORT (Year, Month, Day) <b>91/2/28</b>
15 PAGE COUNT <b>6 pp, 1 table, 3 fig</b>				
16 SUPPLEMENTARY NOTATION				
17. COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number) <b>C60 on CaF<sub>2</sub> - ultra-high vacuum - luminescence - low-temperature absorption spectrum - vibronic splittings - transition intensity mechanism</b>	
FIELD	GROUP	SUB-GROUP		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)  <b>Solid films of C<sub>60</sub> deposited on CaF<sub>2</sub> under ultra-high vacuum show luminescence in the 700-1100 nm spectral range at 20K. A 1400 cm<sup>-1</sup> progression in the a<sub>g</sub> soccerball inflation mode is observed. The low-temperature absorption spectrum exhibits similar fine structure. The characterization of vibronic splittings in the ground and emitting state and the transition intensity mechanism are discussed.</b>				
20 DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION <b>UNCLASSIFIED</b>	
22a NAME OF RESPONSIBLE INDIVIDUAL <b>R. Stanley Williams</b>			22b TELEPHONE (Include Area Code) <b>(213) 825-8818</b>	22c OFFICE SYMBOL <b>UCLA</b>

## Luminescence and Absorption Spectra of C<sub>60</sub> Films

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### Abstract

Solid films of C<sub>60</sub> deposited on CaF<sub>2</sub> under ultra high vacuum show luminescence in the 700-1100 nm spectral range at 20K. A 1400 cm<sup>-1</sup> progression in the a<sub>g</sub> soccerball inflation mode is observed. The low temperature absorption spectrum exhibits similar fine structure. The characterization of vibronic splittings in the ground and emitting state and the transition intensity mechanism are discussed.



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The recent report that the spherical all-carbon molecule  $C_{60}$  can be made in high yield in a carbon arc<sup>1-4</sup> has stimulated new interest in its molecular and spectroscopic properties.<sup>1-8</sup> This new allotrope of carbon has a graphitic closed cage structure consisting of twelve five-membered rings separated by twenty benzenoid six-membered rings. The molecule, which contains 60 atoms lying at the vertices of a truncated icosahedron, is known as Buckminsterfullerene because the geodesic structures of Buckminster Fuller led to the initial proposal of its structure.<sup>9</sup> Solutions of  $C_{60}$  are magenta; the long wavelength absorption edge lies at about 620 nm.<sup>3</sup> It has been reported that no luminescence can be detected at room temperature in solution.<sup>6</sup> The triplet-triplet absorption spectrum has been reported.<sup>6</sup> We report here that films of  $C_{60}$  are luminescent in the 700-1100 nm region at low temperature.

Films of material were grown in an ultra-high vacuum chamber.<sup>7</sup> The starting material was made by the method of Krätschmer and Huffman and purified by passing it through an alumina column.<sup>1</sup> The  $C_{60}$  was placed in a 2cc quartz crucible which in turn was inserted into a pyrolytic boron nitride crucible. The entire chamber was baked so that the temperature of the crucible would not exceed 240°C in order to eliminate any high vapor pressure contaminants from the starting material. The base pressure of the system after bakeout was  $5 \times 10^{-9}$  torr. To initiate the growth, the crucible was heated to about 300°C and the ambient temperature  $CaF_2$  substrate was positioned within the flux of the material 1.5 cm from the face of the crucible. During the initial stages of growth, the thin films were a deep blue; thicker films appeared more brown. The films were stored in vacuo and were only exposed to the atmosphere for minutes during transfer to the spectroscopic instruments.

Electronic absorption spectra of the films were obtained by using an instrument described previously.<sup>10</sup> The sample was mounted on an OFHC copper block in the vacuum shroud of an Air Products displax closed cycle helium refrigerator and cooled to about 20K. The spectrometer resolution was about 5 Å. The emission spectra were obtained from samples mounted in the same displax using an emission spectrometer described previously.<sup>11</sup> The films were excited at wavelengths ranging from 351 nm to 633 nm. The emitted light was collected by using an RCA C31034 photomultiplier or a cooled germanium detector. The spectrometer resolution varied with the slit width used from sample to sample but was always better than 10 Å and 50 Å for the spectra

detected with the photomultiplier tube and the germanium detector, respectively. All emission spectra were corrected for the system response.

The absorption spectrum of a film about  $1\mu\text{m}$  thick on  $\text{CaF}_2$  at 20K is shown in Figure 1. The spectral region shown covers the absorption transition to the lowest energy excited state responsible for the luminescence (vide infra). The onset of absorption occurs at about  $14,500\text{ cm}^{-1}$ ; a weak feature at  $14,420\text{ cm}^{-1}$  is somewhat tentatively assigned as the electronic origin ( $E_{00}$  in Figure 1). The first well resolved vibronic peak is observed at  $14,870\text{ cm}^{-1}$ . The positions of the vibronic bands are listed in Table 1. The spectrum is dominated by pairs of bands (a peak and a higher energy shoulder). The separation between the peak and the shoulder is  $230\text{ cm}^{-1}$ . Spectra measured at room temperature are in good agreement with a previously reported spectrum of  $\text{C}_{60}$  on quartz.<sup>1</sup> It is interesting to note that the low temperature absorption spectrum of the film reported here is very similar to that of  $\text{C}_{60}$  in a frozen glass at 77 K except that the first band in the glass spectrum is found at  $16,200\text{ cm}^{-1}$ .<sup>8</sup> The  $1300\text{ cm}^{-1}$  blue shift of the glass spectrum may be a result of the different dielectric constants of the media. In the glass spectrum, the average separation between the peaks comprising the pairs is  $235\text{ cm}^{-1}$ . An interpretation of the fine structure in the absorption spectra of solid  $\text{C}_{60}$  is indicated in Figure 1. Two vibronic origins a and b, at  $450\text{ cm}^{-1}$  and  $680\text{ cm}^{-1}$  higher energy, are built on the electronic origin  $E_{00}$  respectively. Their energy difference gives rise to the  $230\text{ cm}^{-1}$  separation of pairs of transitions. Both a and b show side bands at  $740\text{ cm}^{-1}$ ,  $1420\text{ cm}^{-1}$  and  $2200\text{ cm}^{-1}$  higher energy. The corresponding side bands are connected by dotted lines in Figure 1. The energy spacings correspond to excited state vibronic splittings that can be roughly compared to ground state Raman frequencies.<sup>5</sup> The  $740\text{ cm}^{-1}$  and  $1420\text{ cm}^{-1}$  intervals correspond to the  $773\text{ cm}^{-1}$  and  $1469\text{ cm}^{-1}$  Raman frequencies, respectively. The frequencies are reduced by about 5% in the excited state. The  $1469\text{ cm}^{-1}$  mode is the totally symmetric soccer ball inflation mode (denoted by the  $\hbar\omega_{ag}$  in Figure 1), whereas the  $740\text{ cm}^{-1}$  mode ( $\hbar\omega_g$  in Figure 1) has gerade parity but is not totally symmetric. The pair of bands observed  $2200\text{ cm}^{-1}$  higher in energy than their vibronic origins each correspond to one quantum of both  $\hbar\omega_{ag}$  and  $\hbar\omega_g$ . Progressions in non totally symmetric modes are often observed in highly symmetric molecules and can be interpreted as a manifestation of the Jahn-Teller effect.

The complete emission spectrum of a film of  $\text{C}_{60}$  at about 20K is shown in Figure 2. The

onset of the first detectable emission occurs at about  $14,500\text{ cm}^{-1}$  and overlaps the onset of the absorption band discussed above. The emission spectrum is not as well resolved as the absorption spectrum, i.e., the peaks are much broader. The breadth is evidence for significant inhomogeneity. The excitation energy migrates among the  $\text{C}_{60}$  chromophores in the solid and emission occurs from a wide variety of different sites, not necessarily from the most abundant ones. The highest energy peak in the emission spectrum occurs at  $14,150\text{ cm}^{-1}$  (Figure 3, top trace). A second resolved peak occurs at  $12,700\text{ cm}^{-1}$ . A shoulder at about  $11,400\text{ cm}^{-1}$  is also observed. The same emission spectra are obtained when the sample is excited at 633 nm (directly into the lowest energy absorption band), 514 nm and 488 nm (into the absorption band with a peak maximum at 450 nm)<sup>3</sup> and 351 nm (into the absorption band with a peak at 330 nm)<sup>3</sup>. The spectral origin of the emission spectra varies slightly from sample to sample. The spectra described above are those with the highest energy origin. Excitation of other samples or regions of the film about  $1\text{ mm}^2$  in size gives rise to spectra which are red shifted by a maximum of about  $500\text{ cm}^{-1}$ . An example is shown in Figure 3. All of the spectra which have been recorded have the same separations between the peaks and shoulders as those described above and shown in Figure 2, and all of the spectra have about the same relative intensities between the peaks and shoulders. This observation excludes the possibility that impurity  $\text{C}_{70}$  emission accounts for one of the two distinct spectra; solid  $\text{C}_{70}$  luminesces at low temperatures in a similar spectral region as  $\text{C}_{60}$  but shows distinctly different fine structure.<sup>12</sup> Analysis of many spectra indicates that most commonly the first peak either occurs at  $14,100\text{ cm}^{-1}$  as discussed above or at  $13,700\text{ cm}^{-1}$ . These spectra are superimposable when the latter is offset by  $400\text{ cm}^{-1}$ . Frequently a superposition of these two spectra were recorded, as shown in the top trace of Figure 3).

The three main vibronic features in the emission spectrum are separated by about  $1400\text{ cm}^{-1}$  as indicated in Figure 2. Because of the width of the resolved bands, the uncertainty is greater than  $\pm 100\text{ cm}^{-1}$ . This progression is assigned to the totally symmetric soccerball expansion mode which has been observed in the Raman spectrum at  $1469\text{ cm}^{-1}$ .<sup>5</sup> There is some evidence for a second progression in the emission spectrum with a separation of about  $800\text{ cm}^{-1}$  which may correspond to the  $740\text{ cm}^{-1}$  progression in the absorption spectrum. However the overlap between the broad bands in the emission spectrum prevents any definitive assignments from being made.

The emitting state has a geometry very similar to that of the ground state, since the progressions observed in absorption and emission have their main intensity in the first two members.<sup>13</sup>

Emission spectra of C<sub>60</sub> in frozen organic glasses at 20 K were studied in order to explore further the medium dependence on the transition energies and the possibility that lattice sites are contributing to the emission spectra of the films. The emission spectra obtained from frozen solutions of 2:2:1 methylcyclohexane : iso-octane : toluene were the same as those obtained from the films. The expected 1300 cm<sup>-1</sup> medium-dependent shift was not observed. These results may indicate that the observed emission originated from microcrystals suspended in the frozen solvent.

The overlap between the onset of the emission and the absorption bands indicates that the same electronic excited state is responsible for both. Molecular orbital calculations suggest that the irreducible representations of the HOMO and LUMO are h<sub>u</sub> and t<sub>1u</sub> respectively.<sup>14</sup> The excited states arising from a one-electron transition are T<sub>1g</sub>, T<sub>2g</sub>, G<sub>g</sub> and H<sub>g</sub>. Transitions from the A<sub>g</sub> electronic ground state are electric dipole forbidden but become vibronically allowed with one quantum of an ungerade vibrational normal mode. An interpretation of the emission and absorption spectra consistent with the above selection rules is that the electronic origin (the energy of the transition between the ground vibrational levels of the electronic ground and excited states) occurs between the first observed peaks in the emission and absorption spectra at about 14,500 cm<sup>-1</sup>. The first observed peaks are thus assigned to one quantum of an ungerade promoting mode. Because the first observed peaks are separated by 720 cm<sup>-1</sup>, the promoting modes involved must be on the order of several hundred wavenumbers. Low frequency modes in this wavenumber range are known, but detailed IR spectra which are required to measure the ungerade modes have not yet been carried out.

### Acknowledgments

We thank Professor Nancy Haegel for the use of the Ge detector. The support of the National Science Foundation (CHE 88-06775) is gratefully acknowledged.

## References

1. Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D.R. *Nature* **1990**, *347*, 354.
2. Krätschmer, W.; Fostiropoulos, K.; Huffman, D.R. *Chem. Phys. Lett.* **1990**, *170*, 167.
3. Ajie, H.; Alvarez, M.M.; Anz, S.J.; Beck, R.D.; Diederich, F.; Fostiropoulos, K.; Huffman, D.R.; Krätschmer, W.; Rubin, Y.; Schriver, K.E.; Sensharma D.; Whetten, R.L. *J. Phys. Chem.* **1990**, *94*, 8630.
4. Haufler, R.E.; Conceicao, J.; Chibante, L.P.F.; Chai, Y.; Byrne, N.E.; Flanagan, S.; Haley, M.M.; O'Brien, S.C.; Pan, C.; Xiao, Z.; Billups, W.E.; Ciufolini, M.A.; Hauge, R.H. Margrave, J. L.; Wilson, L.J.; Curl, R.F.; Smalley, R.E. *J. Phys. Chem.* **1990**, *94*, 8634.
5. Bethune, D. S.; Meijer, G.; Tang, W.C.; Rosen, H.J. *Chem. Phys. Lett.* **1990**, *174*, 219.
6. Arbogast, J.W.; Darmanyan, A.P.; Foote, C.S.; Rubin, Y.; Diederich, F.N.; Alvarez, M.M.; Anz, S.J.; Whetten, R.L. *J. Phys. Chem.*, in press.
7. Tong, W.M.; Ohlberg, D.A.A.; You, H.K.; Williams R.S.; Anz, S.J.; Alvarez, M.M.; Whetten, R.L.; Rubin, Y.; Diederich, F.N. *J. Phys. Chem.*, in press.
8. Whetten, R.L.; Alvarez, M.M.; Anz, S.J.; Schriver, K.E.; Beck, R.D.; Diederich, F.N.; Rubin, Y.; Ettl, R.; Foote, C.S.; Darmanyan, A.P.; Arbogast, J.W. *Mat. Res. Soc. Symp. Proc.*, in press.
9. Kroto, H.W.; Heath, J.R.; O'Brien, S.C.; Curl, R.F.; Smalley, R.E. *Nature* **1985**, *318*, 162.
10. Chang, T.H.; Zink, J.I. *J. Amer. Chem. Soc.* **1984**, *106*, 287.
11. Tutt, L.W.; Zink, J.I. *J. Amer. Chem. Soc.* **1986**, *108*, 5830.
12. Reber, C.; McKiernan, J.; Yee, L.; Zink, J.I., unpublished observations.
13. Yersin, H.; Otto, H.; Zink, J.I. Gliemann, G. *J. Amer. Chem. Soc.* **1980**, *102*, 951.
14. Haddon, R.C.; Brus, L.E.; Raghavachari, K., *Chem. Phys. Lett.* **1986**, *125*, 459.



**Table 1**Transition energies and assignments for the low temperature absorption spectrum of C<sub>60</sub> in Figure 1.

transition energy [cm <sup>-1</sup> ]	difference [cm <sup>-1</sup> ]	assignment
14,420		electronic origin E <sub>00</sub>
14,870	230	vibronic origin a
15,100		vibronic origin b
15,640	240	a + $\hbar\omega_g$
15,880		b + $\hbar\omega_g$
16,260	240	a + $\hbar\omega_{ag}$ , a + 2 $\hbar\omega_g$
16,500		b + $\hbar\omega_{1g}$ , b + 2 $\hbar\omega_g$
17,100	220	a + $\hbar\omega_g$ + $\hbar\omega_{ag}$
17,320		b + $\hbar\omega_g$ + $\hbar\omega_{ag}$

## Figure Captions

### Figure 1

The 20 K absorption spectrum of solid C<sub>60</sub> deposited on CaF<sub>2</sub>. For the assignment of the fine structure see text and Table 1.

### Figure 2

20 K luminescence spectrum of solid C<sub>60</sub> deposited on CaF<sub>2</sub> taken with a Ge detector,  $\lambda_{\text{exc}} = 514$  nm. The main progression in the totally symmetric a<sub>g</sub> mode at an interval of 1400 cm<sup>-1</sup> is indicated.

### Figure 3

20 K luminescence spectrum of solid C<sub>60</sub> deposited on CaF<sub>2</sub> taken with a photomultiplier. The two spectra were obtained from two different regions of the sample. Top trace:  $\lambda_{\text{exc}} = 351$  nm; bottom trace:  $\lambda_{\text{exc}} = 488$  nm.

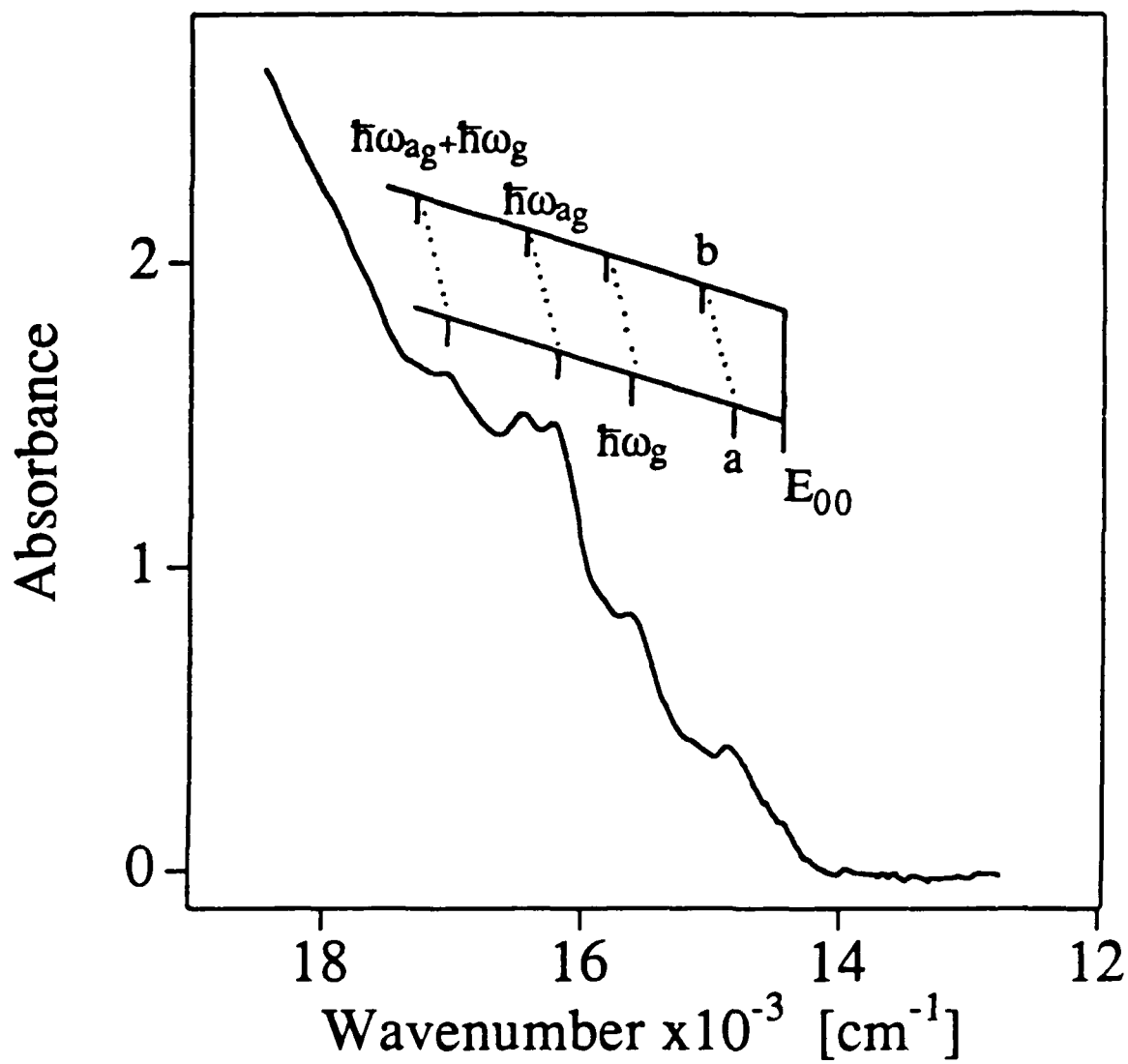


Figure 1

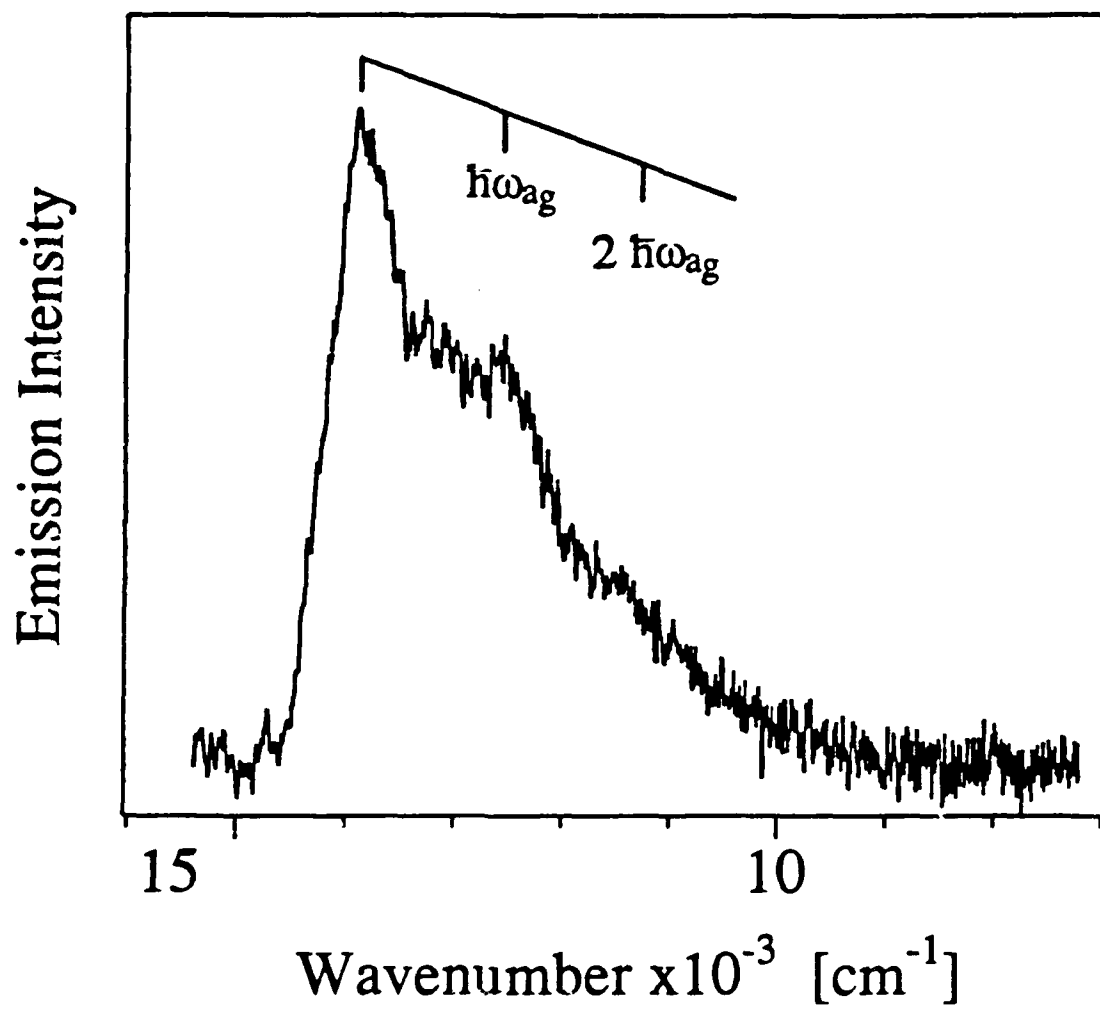


Figure 2

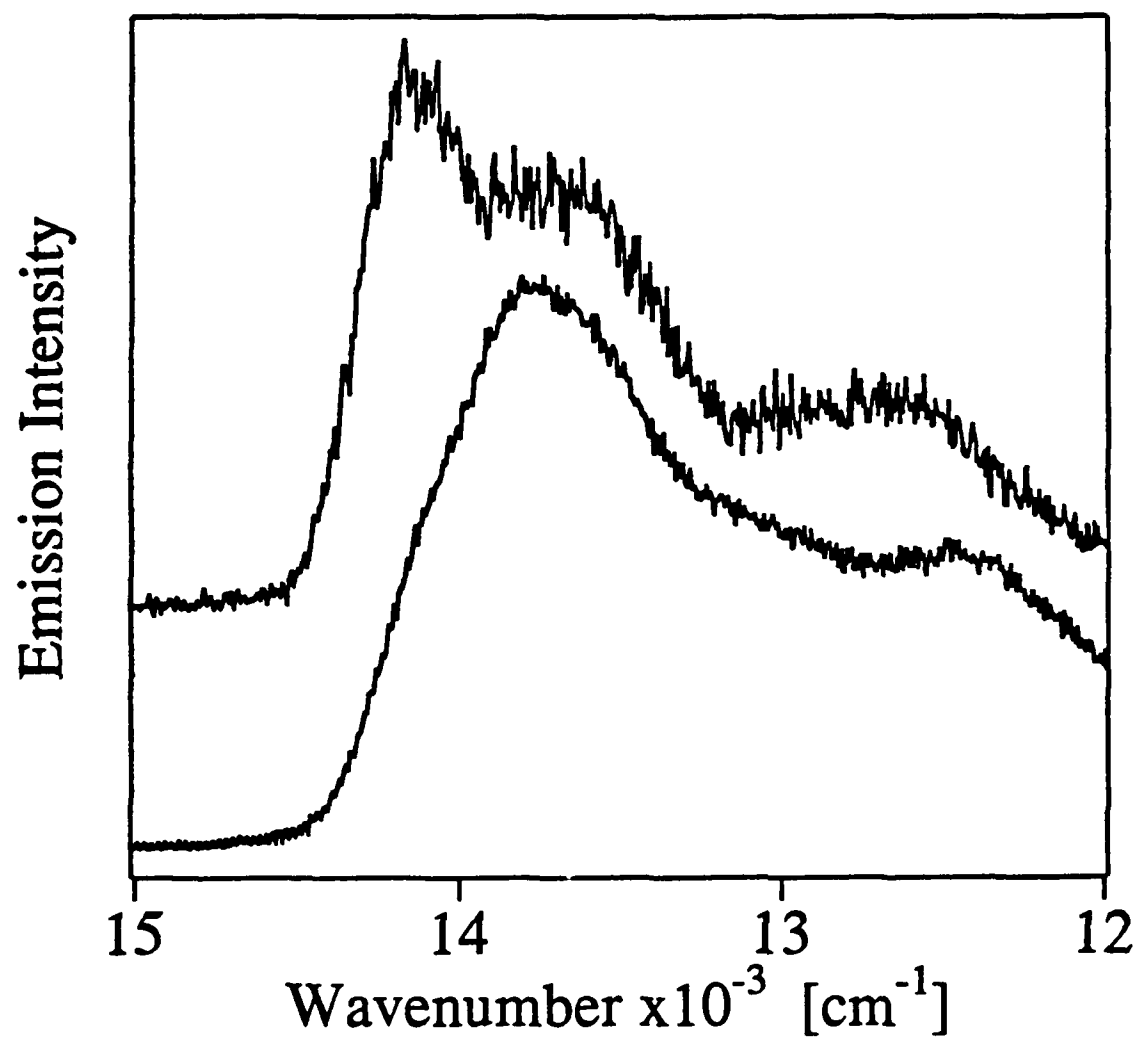


Figure 3